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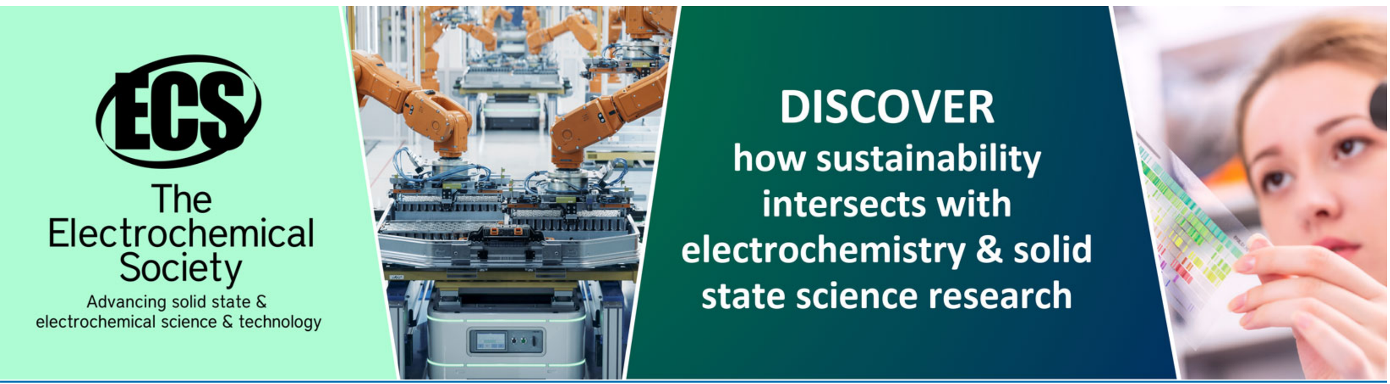

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Investigating the Effect of Doping and Sulfuric Acid (H_2SO_4) on the Growth and Properties of a Triglycine Sulfate (TGS) Crystal

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Abstract. Triglycine Sulfate (TGS) single crystal were grown using a slow evaporation method utilizing deionized water as a solvent at room temperature in two groups. The first group of crystals was grown in a variable pH medium. The second group consisted of crystals doped by Al ions with a varying concentration ratio. It was found that all the TGS crystals grown belong to the monoclinic system, as confirmed through XRD patterns. The results from UV-Vis analysis showed that the crystals grown in the acidic medium were more transparent with increased transmittance to visible light. In addition, the spectral patterns for the as-grown crystals were studied using the FTIR technique, which showed a slight shift, indicating that all the crystals had a similar crystalline structure. The high transmission in the entire visible region for all crystals indicates potential for use of such crystals in (SHG) devices and applications based on UV tunable lasers.
Keywords: TGS, Single crystal, Al ion, Acidic medium, Optical properties.

1. Introduction

The basis of various technology advancements is crystal growth. Control of the crystal grown during crystallization is very important to the industry [1,2]. Triglycine sulfate (TGS) is a ferroelectric crystal that was discovered in 1956 by Mathias Miller and Remeika [3]. TGS is widely used in a wide range of applications, including FTIR spectrometers, where the TGS crystal plays a major role in FT-IR devices and infrared detectors for detection of high detectivity indoor [4]. It is also used for manufacturing capacitors, power transformers and sensors [5]. In addition, (TGS), is have known the best materials of pyroelectric at RT [6]. Wood et al. who revealed that the TGS crystal belongs to the monoclinic system linked with the space group P21 in the ferroelectric phase, and crystallizes in the paraelectric phase linked with the space group P21/m studied the TGS crystal structure. The lattice parameters of TGS crystal are (a = 0.941 nm, b = 1.264 nm, c = 0.57 nm), and (β = 110.13°) [7, 8]. At room temperature, pure TGS crystals have some drawbacks such as easy depolarization by thermal and electrical means, the ferroelectric properties possessing high mobility, low Curie temperature, and contamination with time during the crystal growth; these disadvantages can be overcome by adding proper impurities (doped) into the TGS lattice [9-11]. Some studies demonstrate that the increasing pH of the solution; can grow crystals at higher growth rates [12]. In the present work, the crystal growth of pure TGS in an acidic medium was studied, including the effect of doped aluminum ions on the process of growth; furthermore, the structural, FT-IR, and optical properties of pure and-doped TGS crystals grown by using a slow evaporation method at RT (25°C) were studied. The grown crystals have been characterized by Fourier transform infrared spectroscopy (FT-IR), XRD analysis using a Shimadzu (6000), Japan with

Cu-K$_\alpha$ (λ = 0.1540 nm), and UV-Visible absorption spectra (UV-Visible 1800 double beam spectrophotometer) in the range of (200-1100) nm.

2. Experimental Procedure

In the present investigation, triglycine sulfate (TGS), aluminum sulfate, concentrated sulfuric acid, and deionized water was used. For the process of preparing triglycine sulfate (TGS), the crystals were grown with different molar concentrations and the best concentration was chosen for the growth of crystals in an acidic medium [13]. Specific drops of concentrated (H_2SO_4) sulfuric acid in 50 mL of deionized water in a 500 mL beaker were added. The solution showed pH= (3, 4, 5, and 6) separately. Then, 0.5 M of triglycine sulfate powder was added to each of the solutions with different pH separately. Then, the beakers were put onto a magnetic stirrer at room temperature with continuous stirring. The beakers have wrapped by perforated paper after the material had completely melted, to rule the process of evaporation and then moved in a secluded far away from vibrations and motion. Good quality crystals were collected following a slow evaporation technique after twenty-seven days. All crystals which grown are shown in Figure (1). Table 1 shows the starting time of crystallization and the size of the grown crystals.

Table 1. The starting time of crystallization and the size of the large crystals grown in an acidic medium.

Samples	Nucleation's time by days	Crystal's growth time by days	Size of the largest crystal (mm^3)
TGS pH 6	14	27	(22.11×18.23×5.49)
TGS pH 5	11	20	(39.32×22.49×5.14)
TGS pH 4	7	16	(14.54×14.26×5.20)
TGS pH 3	6	16	(10.76×9.63×4.22)

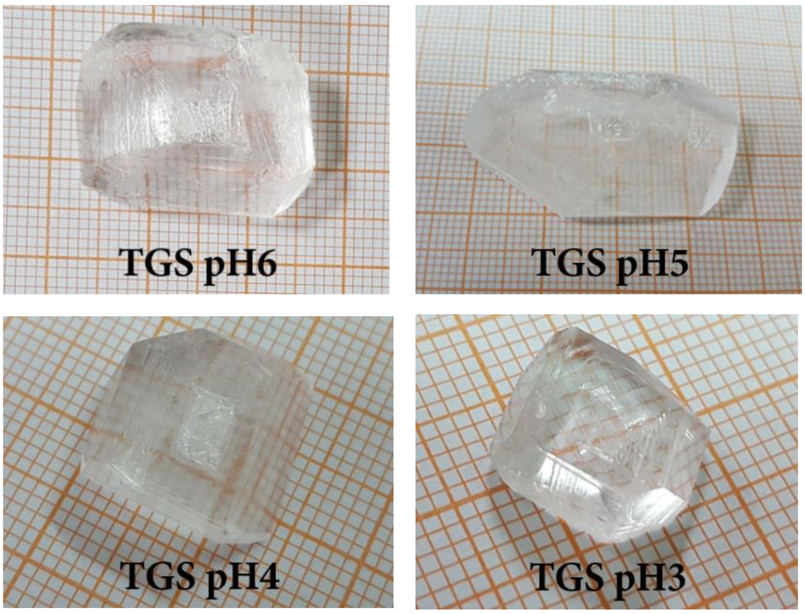

Figure 1. Photograph of a pure TGS crystal, which was grown in an acidic medium.

Figure (2) exhibits the grown crystals. To obtain TGS crystals doped with aluminum ions, ratio (0.001, 0.003, 0.005, 0.007, 0.01) M has been added up to the solution of triglycine sulfate individually, by using a slow evaporation method, after twenty-three days, the grown crystals have collected. Those as-grown crystals are observed in Figure (2). Table 2 shows the size of the as-grown crystals, the start of nucleation and the time of the crystallization

Table 2. The size of the large TGS crystals doped with Al ions and time of crystallization process.

Sample	Nucleation's time by days	Crystal's growth time by days	Size of the largest crystal (mm^3)
TGS Pure	14	27	(15.10×10.21×3.50)
TGS:0.001Al	10	23	(15.15×13.73×4.11)
TGS:0.003Al	10	23	(11.75×10.64×4.02)
TGS:0.005Al	8	21	(30.87×12.47×5.89)
TGS:0.007Al	7	21	(20.79×19.52×30.7)
TGS:0.01Al	5	18	(13.64×10.12×3.23)

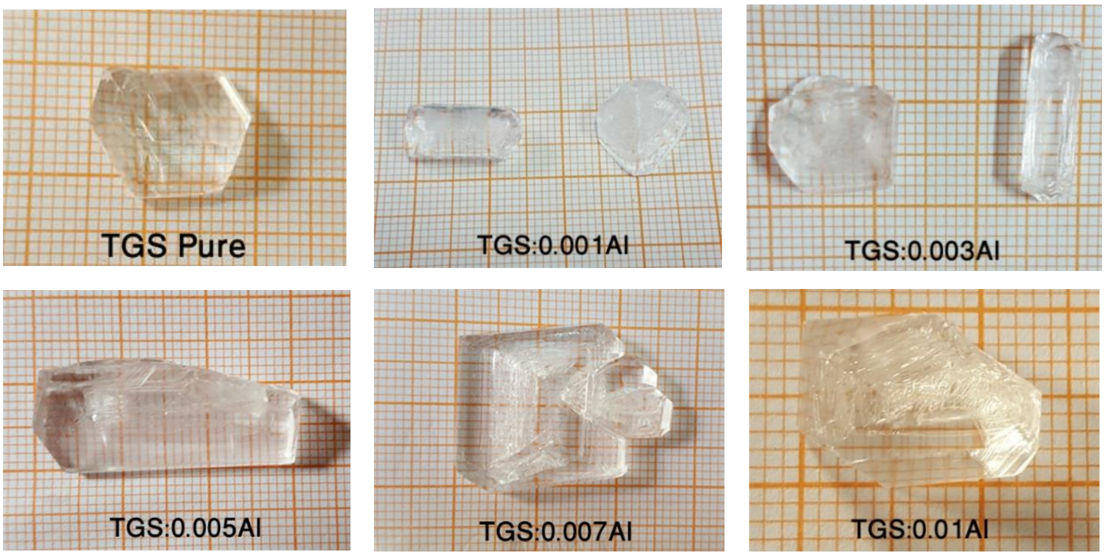

Figure 2. The photograph of a triglycine sulfate crystal doped with Al ions.

3. Results and Discussion

3.1. Crystal Growth

It can be seen that the crystals were obtained through spontaneous nucleation of the mother solution by slow evaporation technology. As observed in the crystals grown in acidic medium, the rate of growth and quality of crystals mainly depends on the pH number: a low pH number in the solution increases the rate of growth and the quality of the crystals as they show good and transparent faces. When the pH number is high, there is a low rate of growth for all faces and phases [14]. Additionally, it was found the largest size for the pure TGS crystal grown in acidic medium was (39.32 × 22.49 × 5.14) mm^3 at pH = 5. A group of researchers has also previously studied the effect of chemistry and materials on the properties of a TGS crystal [14]. In the present study, the effect of aluminum ions on the growth conditions and the shape of the crystals was observed, where the doped crystals were found to show full faces, and the others remain unfinished relying on the growth conditions. An increase in the growth rate was observed with increasing dopant concentration, especially at the ratio of 0.01%. It is obvious that there is a relationship between the ratio of doped ions and the rate of growth: the higher the ratio of doped ions the lower the growth time. In general, all the pure TGS crystals grown in an acidic medium and doped with aluminum ions were of good quality, optically transparent and with a stable quality.

3.2. XRD Analysis

The as-grown pure TGS crystals in the acidic medium doped with aluminum ions were studied by XRD analysis; in addition of that, the "fullprof" software, that depends on Rietveld analysis, was applied to obtain more accurate values for the parameters of unit cell from the patterns of all the crystals [15,16]. Figure (3) shows the diffraction patterns of pure triglycine sulfate crystals growing in an acidic medium for the angle range (10°- 40°) The detected peaks in all XRD patterns for the pure crystals in an acidic medium show that they correspond well with the JCPDS data (file 14-0873). The lattice constants for pure crystals in the acidic medium were compared with the results in the mentioned file; these results are shown for all samples in Table (3). From Figure (3), it can be observed that the highest intensity peaks with pH=6 occur at (2θ ~ 26 °), which corresponds to the $(\bar{1}31)$ plane. For the sample with pH=5, the highest peak can be seen at (2θ ~ 38°), corresponding to the $(\bar{2}32)$ plane. For TGS crystals pH 4 and pH 3, higher intensity peaks can be seen at (2θ ~ 28°) and (2θ ~ 32°) respectively, which correspond to the (040) and $(\bar{1}41)$ planes, respectively. The explanation for the occurrence of this difference in the intensity of the peaks is due to the preferential orientation.

Table 3. Unit cell parameters for TGS crystals grown in an acidic medium.

Crystal Pure	a (nm)	b (nm)	c (nm)	β (deg)	Cell volume $(nm)^3$
Standard JCPDS	0.9417	1.2643	0.5735	110.23	0.682804
TGS pH 6	0.92036	1.26263	0.57144	105.51	0.664056
TGS pH 5	0.92345	1.26243	0.57269	106.05	0.667637
TGS pH 4	0.91609	1.26595	0.57253	105.15	0.663977
TGS pH 3	0.91597	1.26242	0.57382	105.26	0.66353

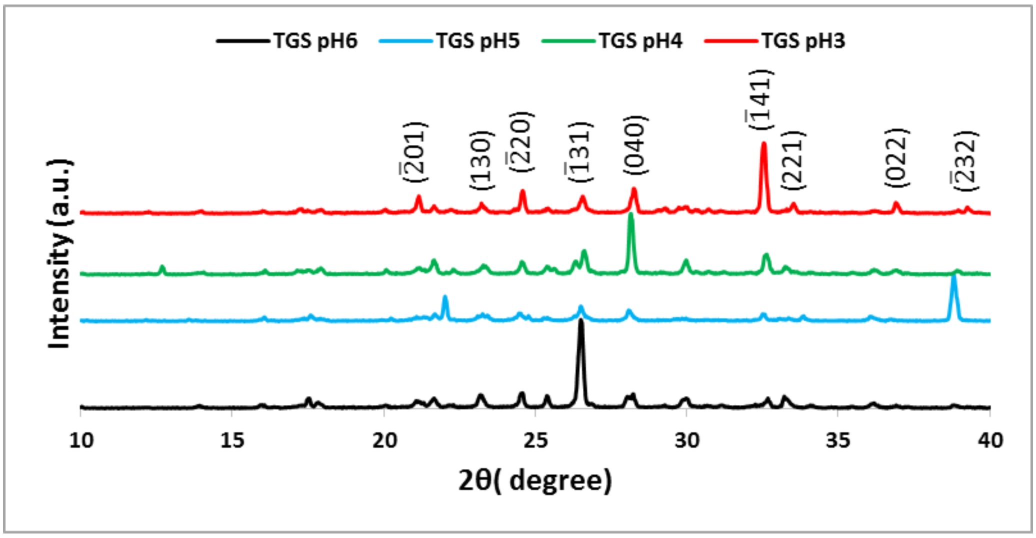

Figure 3. XRD patterns for pure TGS crystals grown in the acidic medium.

From Figure (4), which represents the diffraction patterns for the pure and aluminum-ion-doped TGS crystals, the peaks observed in all XRD patterns for all samples show that they correspond well with the JCPDS data (file 14-0873). The lattice constants for the pure and-doped TGS crystals were compared with the results in the mentioned file; these results are shown for all samples in Table (4).

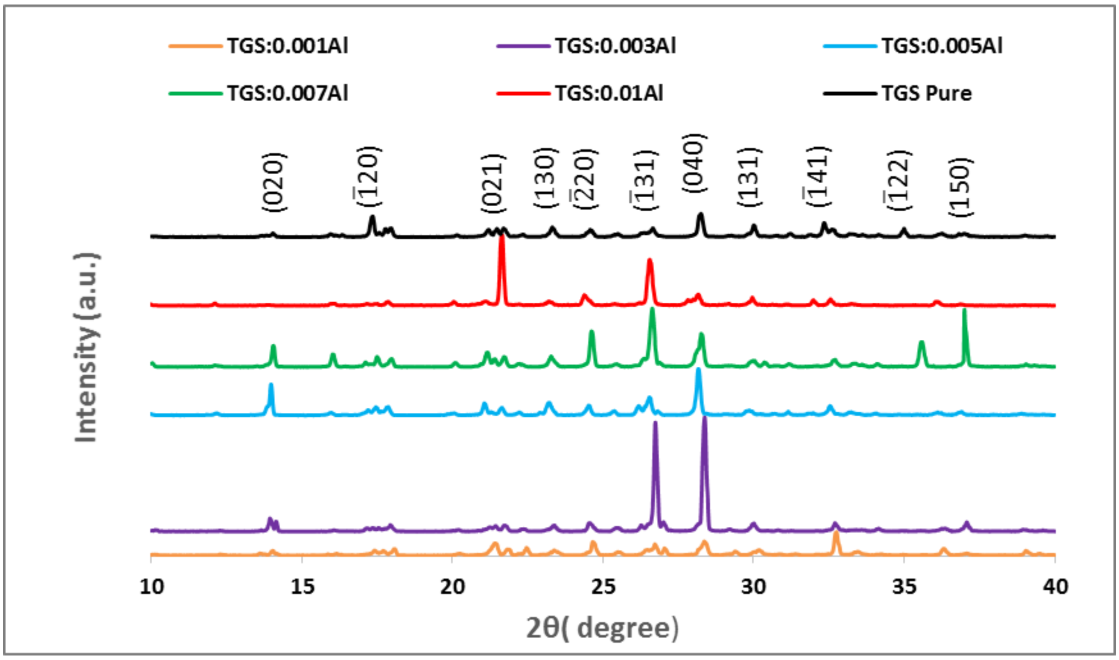

Figure 4. XRD patterns for TGS crystals doped with Al ions.

Table 4. Unit cell parameters for TGS crystals doped with Al ions.

Crystal	a (nm)	b (nm)	c (nm)	β (deg)	Cell volume $(nm)^3$
Standard JCPDS	0.9417	1.2643	0.5735	110.23	682.8041
Pure TGS	0.9153	1.2684	0.573	105.59	665.2338
TGS:0.001Al	0.91657	1.26492	0.57653	106.43	668.4218
TGS:0.003Al	0.91685	1.27577	0.57328	106.42	670.5597
TGS:0.005Al	0.91685	1.27577	0.57428	106.34	671.7294
TGS:0.007Al	0.91695	1.27577	0.57498	106.15	672.6216
TGS:0.01Al	0.92665	1.26566	0.57405	105.79	673.2595

It can be observed that the positions of the peaks are unchanged but the intensity of the peaks vary because of the presence of a preferential orientation of the crystal growth for the surface at the expense of another surface [17]. This is due to the type of bond formed by the atoms or the specific heat of the solid body or the difference in the melting points of the components of the substance or thermodynamic properties [18]. The difference in intensity of the measured peaks is mainly related to changes in the diffusion density of the crystal structure components and their arrangement in the lattice [19]. A change happened in the lattice constants for crystals doped with aluminum ions from one specimen to another corresponding to the rate of doping. Therefore, the size of the unit cell has become greater than it was before doping because the aluminum ion with a radius of (0.53) Å replaces sulfate ions with a radius of (0.37) Å, which is smaller than the radius of the doped ions. As a result, the substitution process increases the size of the cell unit for-doped TGS crystals [20, 21]. All diffraction patterns for pure and-doped TGS crystals in acidic medium were observed to belong to the monoclinic system and to the space group ($P2_1$). The unit cell diagram and the atom locations for the triglycine sulfate crystal were determined using "VESTA", as shown in Figure 5.

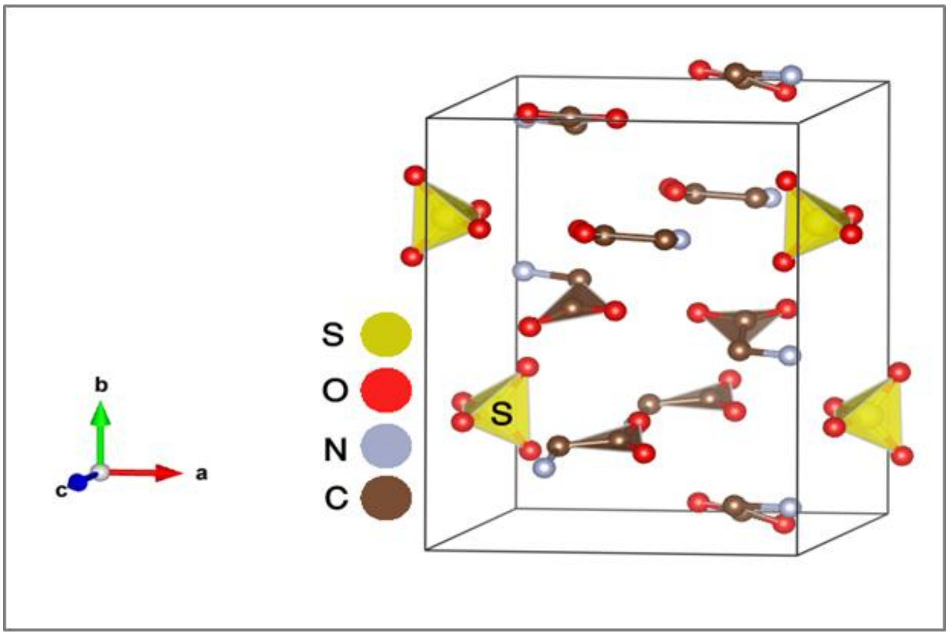

Figure 5. Unit cell diagram of the TGS crystal.

3.3. Analysis of UV-Visible Spectral

The optical transmittance spectra for the as-grown crystals have been measured using a UV-Visible 1800 (Shimadzu) in the wavelength range (200-1100) nm, which covered the full near- ultraviolet, visible, and near-infrared region. This enables one to determine the transmittance range capability for these crystals for different optical applications. From Figure (6), one observes that the transmittance slightly increases with increasing pH, with the transmittance reaching approximately 75.15%. As observed from Figure (7), which represents the transmittance spectrum of TGS crystals doped with aluminum ions, the transmittance decreases for increasing doping rates, reaching approximately 72.13% for the pure crystal and decreasing with increasing vaccination until reaching approximately 63% at TGS 0.01. The good transmittance and absorption's absence of in the fully visible region makes these grown crystals suitable for use in optoelectronic applications, as confirmed by some previous papers [22-24]. In contrast, the high transmission in the entire visible region for the Al-ion-doped TGS crystal displays potential for using this as-grown crystal in a second harmonic generation (SHG) device and applications based on UV tunable lasers [25].

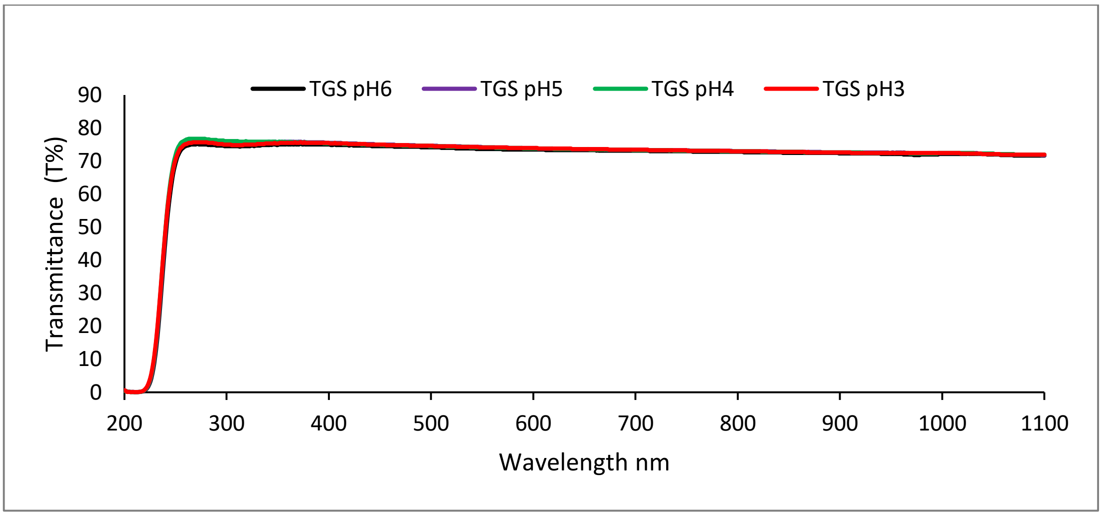

Figure 6: The transmittance (T %) spectra for pure TGS crystals in the acidic medium.

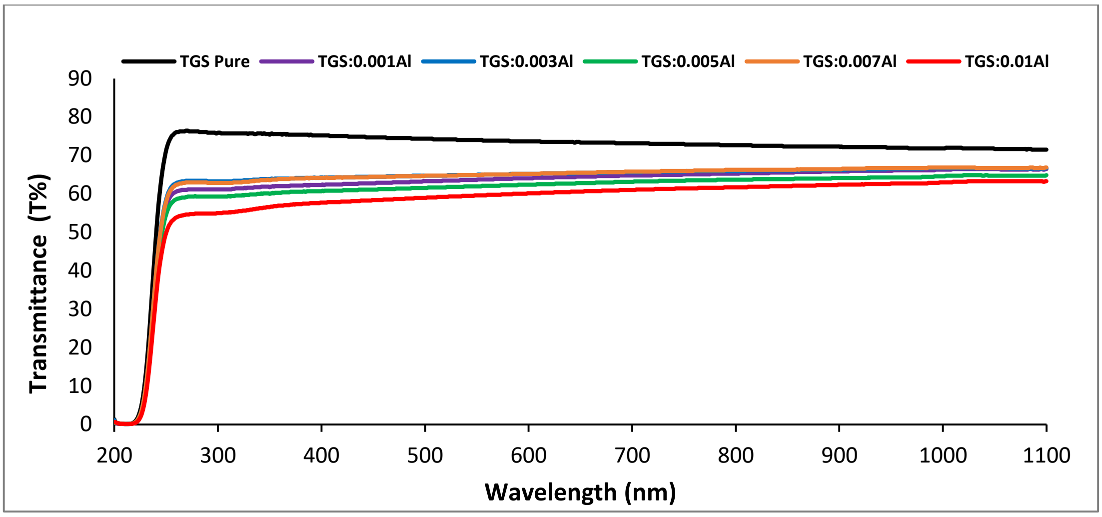

Figure 7: The transmittance spectra (T %) for pure and-doped TGS crystals.

3.4. Analysis of FT-IR spectroscopy

FT-IR was recorded in the range (400- 4000) cm^{-1} employing a (BRAC)-WQF-520. Figure (8) and (9) show the resulting spectra for pure and-doped TGS in an acidic medium. The pure TGS crystals in the acidic medium show a wide and strong absorption in the range of (3800-3006) cm^{-1} resulting from OH stretching and OH extension and show an absorption due to CH_2 in the range (2925-2607) cm^{-1}. The infrared peaks observed in the region between (1716) cm^{-1} and (1869) cm^{-1} corresponding to the extension of the vibration of C = O indicate the presence of a glycinium ion [26]. For the peak at (1500) cm^{-1}, it is attributed to the curvature of the NH_3^+; the peak at 1018 cm^{-1} is due to the vibration of the SO_4 family. There is also an absorption at 904 cm^{-1}, which results from the C-C expansion. It is obvious that all the vibrational patterns for the pure TGS crystals confirm the presence of active groups in the grown crystals, which is well compatible with a number of sources [27,28]. For the doped TGS crystals, there are references to wide bands and small shifts, which confirm the presence of an impurity in the doped crystals [29].

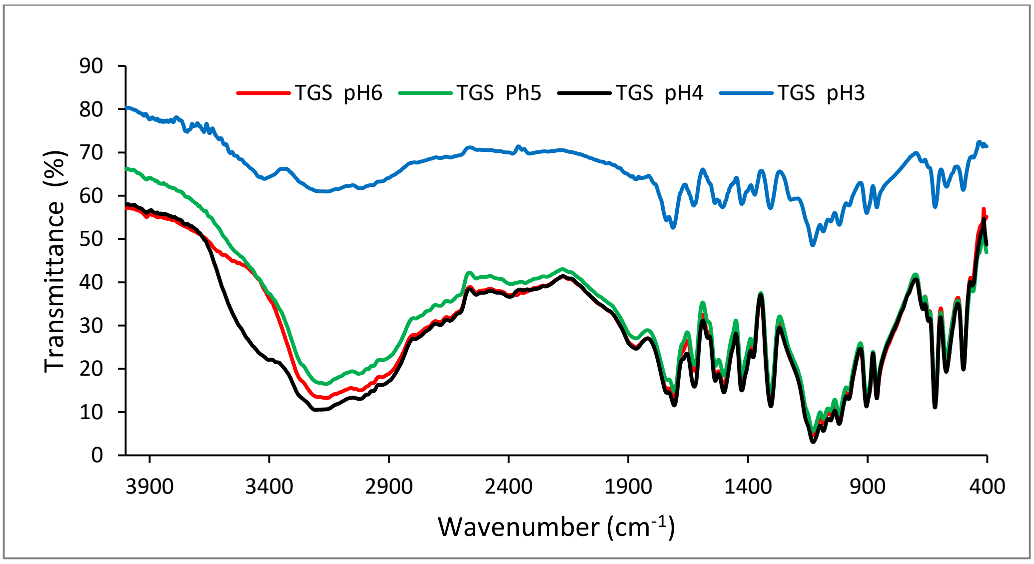

Figure 8. FTIR spectra for pure TGS crystals grown in different acidic media.

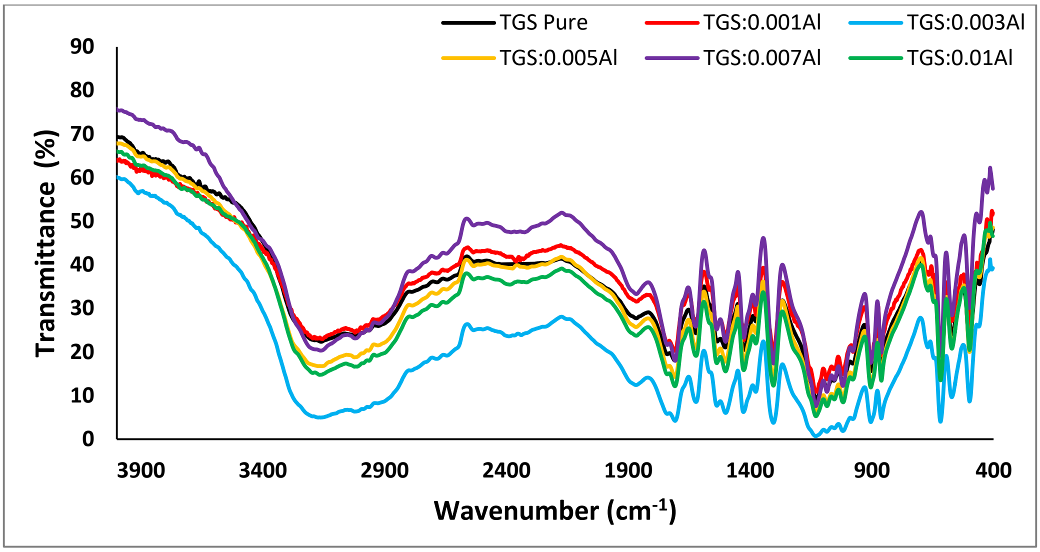

Figure 9. FTIR spectra for pure and aluminum-ion-doped TGS crystals.

4. Conclusions

Single crystal growth of pure and aluminum-ion-doped triglycine sulfate in an acidic medium was successfully realized by a slow evaporation method utilizing deionized water as the solvent at room temperature. It was observed that the rate of growth and quality of the crystals mainly depended on the pH number; also, the rate of growth depended on the rate of doping; the ideal time nucleation starting process was 5 days, with growth completion occurring at 18 days at a doping rate of 0.01%. X-ray analysis disclosed that the pure triglycine sulfate crystals grown in acidic medium and the doped with Al ions belong to the monoclinic crystal structure. UV-Visible spectra demonstrate that in the visible region, the grown crystals have high transparency. The spectral patterns for the as-grown crystals were measured using FTIR technology and were found to be similar to those obtained for the undoped crystals, with a slight shift indicating that all crystals had a similar crystalline structure.

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